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Overview of Analytical Techiques for Herbicides in Food

Hua Kuang, Libing Wang and Chuanlai Xu
Jiangnan University
China

1. Introduction

It is said that there are more than 5800 kinds of weeds, which significantly do harm to the agricultural production and weed control has always been an important issue in agrochemical practice. Chemical agents, that is herbicides, are used widely in the world in protecting crops from undue competition from weeds.

The main chemical classes of herbicides(Tadeo et al., 2000) include bipiridilium compounds, triazine derivatives containing three heterocyclic nitrogen atoms in the ring structure (atrazine, prometryn, propazin, etc.), chlorophenoxy acid derivatives (2, 4-D, 2, 4, 5-T), substituted chloro-acetanilides (alachlor, propachlor), derivatives of 2, 6-dinitroaniline (benfluralin, trifluralin), substituted phenylcarbamates (carbetamide, chlorbufam), urea derivatives (chlorbromuron, chlorotoluron), substituted sulphonylureas (amidosulfuron, trifusulfuron), etc. The intensive application of herbicides has resulted in the contamination of the atmosphere, soil and waste water, agricultural products (wheat, corn, fruits, vegetables, beans etc.) and, consequently, in the direct or indirect pollution of food and food products and biological system.

More studies have shown that herbicides or its metabolites can enter into the human body along food chain, which creates potential health risks to human. Growing concern has been taken for this issue and some herbicides have been banned to use (see table 1).

The development of a robust analytical method is a complex issue. All steps in the analytical process including sample preparation, extraction, cleanup and instrumental analysis are equally important. There are a vast series of techiniques to use in establishing analytical methods, however, some rules should be taken for the differences in polarity of herbicides and the type of sample matrix. The objective of this paper is to summarize the anlytical measures developed to detect the different classes of herbicides residues in various foods, and to review future trends.

2. Phenoxycarboxylic acid herbicides

The herbicidal effect of 2, 4-D was first discovered by Amchem company in 1942 (Kuang et al., 2006b), and more categories were developed by a lot of companies since 1945 based on the structure of 2, 4-D. The general formula of this class herbicides see fig 1 and the chemical structure of some most used phenoxycarboxylic acid herbicides were summarized in table 2. 2, 4-D is the world's largest broad-leaved weed herbicides. Phenoxycarboxylic acid

Class of Herbicides	EU	U. S. A	Japan	China
Phenols	Dinoterb 2-Methyl-4, 6-Dinitrophenol (DNOC) Pentachlorophenol	Dinoseb DNOC	Dinoterb Pentachlorophenol	Dinoterb DNOC Pentachlorophenol
Ureas	Monolinuron Chloroxuron Difenoxuron Noruron Chlorbromuron Cycluron Dimefuron Momuron Neburon Tebuthiuron Thiazafluron Benzthiazuron Ethidimuron Metobromuron Metoxuron Fenuron	-	Chloroxuron Monolinuron Tebuthiuron Benzthiazuron	-
Amides	Metolachor Butachlor Monalide Diethatyl-Ethyl Mefenacet Tebutam Isocarbamide Diphenamide Chlorthiamid Pentanochlor Flamprop Flupoxam	Metolachor	Metolachor Butachlor Mefenacet Flamprop	
Triazine	Propazine Ametryn Aziprotryne Desmetryne Methoprothryne Trietazine Terbumeton Secbumeton Cyanazine Terbutryn Hexazinone Prometryn	Propazine Ametryn Cyanazine Hexazinone	Propazine Tebutryn	-

Class of Herbicides	EU	U. S. A	Japan	China
Dinitroaniline	Dinitramine Isopropalin Nitralin	Nitralin	-	-
Diphenyl Ethers	Fluoroglycofen Fluorodifen Acifluorfen Fomesafen Chlormethoxyfen	Acifluorfen	Fomesafen	Acifluorfen Fomesafen
Carbomates	Cycloate Vernolate Dimepiperate Dimexano Propham Butylate Chlorbufam Tiocarbazil Karbutilate Di-Allate Barban S-Ethyl-N, N-Dipropylthiocarbamate(EPTC) Orbencarb Pebulate	Propham Cycloate Butylate Pebulate	Cycloate Butylate Pebulate	-
Phenoxycarboxylic Acids	Fluazifop Quizalofop Fenoxaprop Haloxyfop 2, 4, 5-T Dichlorprop Fenoprop 2, 3, 6-Trichlorobenzoic Acid (2, 3, 6-TBA)	Fenoprop	2, 4, 5-T	2, 4, 5-T Fenoprop
Imidazolinones	Chloramben Imazamethabenz Imazapyr	-	Imazamethabenz Imazapyr	-
Cyclohexanediones	Sethoxydim Alloxydim	Sethoxydim	-	-
Others	Chlorfenprop-Methyl Allalacohol Benazolin Benzoylprop Bensulide Bromofenoxim Dalapon	Bensulide MSMA Norflurazon Benfuresate Bromacil	Bensulide Flamprop Pyrazoxyfen TCA Bromacil Naptalam	Bromacil

Class of Herbicides	EU	U. S. A	Japan	China
	Endothal			
	Flamprop			
	Fluridone			
	Flupoxam			
	Methazole			
	Sodium Hydrogen Methylarsenate (MSMA)			
	Norflurazon			
	Perfluidone			
	Pyrazoxyfen			
	Trichloroacetic Acid (TCA)			
	Tridiphane			
	Benfuresate			
	Bromacil			
	Naptalam			

Table 1. List of banned herbicides in various countries

R1= CH2, CH3 (CH2)n, (CH2)n

R2=Cl, CH3

R3= Cl, -O-pyridine

R4= Cl
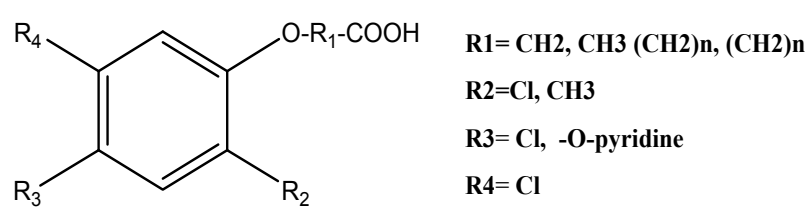
Fig. 1. Parent Chemical Structure of Phenoxycarboxylic Acid Herbicides

herbicides have been used intensively in the control of the growth of grass and the broad-leaf weeds in many crops such as paddyfield, wheat, soybean, etc.

Due to their solubility in water, these herbicides are easy to migrate in agricultural ecosystem causing the pollutions of soil, groundwaters, and air. Phenoxy acid herbicides are medium toxicity themselves, but their metabolic products (especially some halids)are harmful to the human and other creatures. Investigations indicate that they could induce the human parenchyma malignancy tumor and embryotoxicity in animals(Kuang et al., 2006a).

2.1 Sample extraction

Since phenoxy acid herbicides show high polarity and are easily dissolved in the water or aqueous-phase solution, phenoxyacids and benzonitriles are widely applied as salts or esters, but they are decomposed rapidly by hydrolysis, in the treated plants, to their respective phenols or acids. Residues of these acidic herbicides are best extracted from foods when a hydrolytic step is included to release the free acidic herbicide from the conjugated products formed with plant components(Rimmer et al., 1996). With this aim, acid or base hydrolysis has been used. For acid hydrolysis process, samples have to be acidified with acid solution transferring the analytical objective into the organic phase. It was reported(Baggiani et al., 2001) that the sample should be acidified with acidification water (pH < 2), then extracted with proper organic solvent-water mixture. Solvents, such as

acetonitrile, toluene-ether, dichloromethane and etc., can be used to extract the phenoxy acid herbicides from matrix. For base hydrolysis, alkaline solution (0.1 M NaOH) was used mostly. Many extraction methods including ultrasonic extraction, shaking extraction, microwave-assisted solvent extraction(MASE) and supercritical fluid extraction(SFE) have been reported (table 3).

2.2 Cleanup
Many components in matrix can be co-extracted in sample extraction step and targeted compounds are generally present in very low concentration, they need to be separated from undesirable substances effectively. Some authors have previously summarized the primary cleanup process on these compounds(Cserháti et al., 2004). Liquid-liquid extraction (LLE) has frequently been used to remove co-extracts from sample constituents. The efficacy of the method is generally high but requires highly purified and expensive solvents. However, serious emulsifying phenomenon sometimes is present during the shaking process. Gel permeation chromatography (GPC) mainly used to remove lipids or colors from extracts based on the differences of molecule size between targeted compounds and interferences. Kuang et al., 2006 sucessefully purified 14 phenoxy acid herbicides (M. W. ranging from 180 to 327) from soybean extracts.

However, the most common approach to cleanup in herbicide analysis now is solid-phase extraction (SPE), sorbents such as aminopropyl(NH₂), reversed-phase (C₁₈), strong cation exchange(SCX) and normal-phase sorbents(florisil, alumina) are very useful for cleaning up complicated extracts (see table 3).

2.3 Detection
2.3.1 Gas chromatography (GC)
Phenoxy acid herbicides benefit poor volatility for its low pka (acid dissociation constant) values (see table 2) and derivatization process is needed when analysis by gas chromatography requires. The most frequently used derivatization reagent is diazomethane;however, due to its toxicity, carcinogenicity and explosiveness, other alternative esterification reagents such as sulphuric acid in 1-propanol or in methanol and boron trifluoride in methanol, n-butanol or 2-chloroethanol have been proposed.

Methylation and PFBBr (pentafluorobenzyl bromide) esterification are common approaches. Methylating agents such as boron trifluoride-methanol, chloroformate, trimethylsilyldiazomethane have been reported in detection of phenoxy acid herbicides (Table 4). Diazomethane was applied for methylation of 6 herbicides (Wei et al., 2005) and satisfying derivative effects obtained. Trimethylsilyldiazomethane, as a non-toxic non-mutagenic1 alternative to diazomethane is widely used in methyl derivatization. The summary in table 4 showed that mainly mass spectrometry and electron capture detector (ECD) were used to detect phenoxy acid herbicides. Other detectors including hydrogen flame ionization detector (FID) and nitrogen-phosphorus detector(NPD) were also reported for analysis. Kuang(Kuang et al., 2006a) found that ECD response of methylated product of phenoxy acid herbicides, especially single-chlorine substituted molecules (MCPA, MCPP, MCPB etc.), was much lower than that of PFBBr ester. A comparison of the response factors between PFBBr ester and methyl ester of MCPA, 2, 4-D and 2, 4, 5-T had been made (Lee et al., 1991). The response factor of the chlorophenoxy herbicide of PFBBr ester was almost 600 times than that of methyl ester.

Name	Chemical Strucutre	CAS. No	pKa
Mecoprop (MCPP)		7085-19-0	3.78
2-Methyl(4-Chlorophenoxy) Acetic Acid (MCPA)		202-360-6	3.07
2-Methyl(4-Chlorophenoxy) Acbutyric Acid (MCPB)		94-81-5	4.84
2, 4-Dichlorophenoxyacetic Acid(2, 4-D)		94-75-1	2.73
2, 4-Dichlorophenobutyric Acid		94-26-8	4.80
Dicamba		1918-00-9	1.97
Fluazifop		69335-91-7	3.20
4-Chlorophenoxyacetic Acid		122-88-3	--
Dichlorprop		28631-35-8	3.00
2-(4-Chlorophenoxy) Propionic Acid		3307-39-9	--
3, 4-Dichlorophenoxyacetic Acid		588-22-7	--
2, 4, 5-(Trichlorophenoxy) Propionic Acid (2, 4, 5-T)		93-76-5	3.14
Fenoprop		93-72-1	3.10
Phenoxy Butyric Acid		6303-58-8	--

Table 2. Information for 14 phenoxy acid herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref
Oranges	2, 4-D	Methanol–homogeniser	-	(Williams et al., 1997)
Fruits, vegetables	2, 4-D	Diethyl ether–hexane (acidic pH), homogeniser	NH_2 cartridge	(TING & Kho, 1998)
Wheat	2, 4-D	Ethanol–water, homogeniser	LLE–Florisil column	(Cessna & Holm, 1993)
Onions	Fluazifop-butyl	CO_2 –SFE	-	(Wigfield & Lanouette, 1993)
Fruits, vegetables	2, 4-D	Methanol–water (basic pH), blender	C_{18} cartridge	(Richman et al., 1996)
Oranges, grapefruits	2, 4-D	Acetonitrile–water, homogeniser	LLE	(Rochette et al., 1993)
Citrus fruits	Dichlorprop	Methylene chloride–acetone, shaker	LC-SCX cartridge	(Peruzzi et al., 2000)
Barley, triticale	Mecoprop, 2, 4-D	0.1 M NaOH, blender Ethanol–water, homogeniser	LLE–Florisil column	(Cessna, 1992) (Sánchez-Brunete et al., 1994)
Wheat, barley	Phenoxyacids	Methanol, homogeniser	LLE–Florisil column	(Su, 1975)
Mushrooms	2, 4-D	Diethyl ether (acidic pH), homogeniser	Alumina column	(Siltanen, 1978)
Wheat	2, 4-D	0.1 M NaOH–diethyl ether–hexane (pH 1), blender	LLE–Florisil column	(Smith, 1984)
Potatoes, soybeans	Fluazipop-butyl	0.1 M NaOH, shaker	LLE–Florisil column	(Clegg, 1987)
Wheat	2, 4-D,	0.1 M NaOH, blender	LLE–Florisil column	(Cessna, 1980)
Soybean	Phenoxyacids	acetonitrile-50mM HCl (v/v 7:3)	LLE- anion exchange column GPC- anion exchange column	(Kuang et al., 2006a; Kuang et al., 2006b)

Table 3. Extraction and cleanup of phenoxy acid herbicides

Reagents	Matrix	Detection system	Ref
Diazomethane	Rice, Soil, water	GC-MS	(Wei et al., 2005); (Hodgeson et al., 1994)
CH$_3$I	Vegetables, water	GC-ECD	(Rompa, 2005)
Dimethyl sulfate	water	GC-MS	(Catalina et al., 2000)
Trimethylsulfonium hydroxide(TMSH)	water	GC-MS	(Neitzel et al., 1998)
Tetramethylammonium hydroxide (TMAH)	Standards	GC-MS	(Brondz & Olsen, 1992)
tetrabutyl ammonium salt，TBA	water	GC-MS	(Ding et al., 2000)
2-cyanoethylmethyldieth N, O-bis(trimethylsilyl)	Standards	GC-NPD	(Bertrand et al., 1987)
trifluoroacetamide, BSTFA	Standards	GC-MS	(Lou et al., 1999)
PFBBr	Water, Soil, rice, air	GC-MS, GC-ECD	(Cserháti & Forgács, 1998); (Tadeo et al., 2000)
Benzyl bromide	water	GC-MS, GC-FID	(Nilsson et al., 1998)
Chloromate	water	GC-MS, GC-ECD	(Butz & Stan, 1993)
Concentrated sulfuric acid	water	GC-MS	EPA Method 8151A
HCl- Acetic Anhydride	water	GC-MS	(Xing et al., 2002)
BF$_3$	Soil, Meat, Rice	GC-MS, GC-ECD	(Sánchez-Brunete et al., 1994)

Table 4. Derivatization method of phenoxy acid herbicides

The requirement of the maximum residue limits (MRLs) of phenoxy acid herbicides was critical, especially in Japan where 2, 4, 5-T can not be detected in foods. Most derivatization products can be separated on weakly polarity [stationary phase of column, (5%-Phenyl)-methylpolysiloxane and medium polarity [(14%-Cyanopropyl-phenyl)-methylpolysiloxane] capillary columns. Because of the similarity of these herbicides between their structures and polarities, slow temperature program-up was needed to acquire an effective separation. A typical programmed temperature is set as follows:

The oven initial temperature 60 °C holding 1 min and was programmed at 25 °C /min to 180 °C, (1min hold), then programmed at 2 °C /min to 205 °C, (3 min hold), finally programmed to 260 °C at 10 °C /min (5 min hold).

2.3.2 High performance liquid chromatogeaphy (HPLC)

Considersing weak volatility of phenoxy acid herbicides, liquid chromatographic separation seems more suitable than gas chromatography. Derivatization, not only is time consuming, but also affects the reproducibility and stability of the method.

Most phenoxy acid herbicides showed maximal UV absorption ranged from 200-220nm, where mighty interference existed and stable baseline often can't be gotten. Thus, some

analysts carried out derivatization process in analysis of these class compounds aimed to change their chromatographic behavior not to improve the detection sensitivity.

Phenoxy acid herbicides showed high polarity with pKa distributed in 2 to 5(Kuang et al., 2006a), the analysts need to adjust the pH of the mobile phase. Organic acids such as acetic acid, trifluoroacetic acid or inorganic acid can be used to adjust the acidity.

The great advantage of HPLC tandem mass spectrometry (HPLC-MS/MS) is its highly selectivity, which greatly reduce the false positive results in detection. Kim (Kim et al., 1991) applied HPLC-MS to detect 2, 4, 5-T, 2, 4-D and fenoprop residues in water, which was the first application of HPLC-MS techniques in phenoxy acid herbicide detection. Ultra Performance Liquid Chromatography (UPLC) employs 1.7 um particles, resulting in a very flat VanDeemter plot and a linear velocity faster than usual one with 5 um packings; consequently, improves resolution, speed and sensitivity for many HPLC methods. Chu, 2008(Chu et al., 2008) realized simultaneous determination of more than 100 herbicides in soybeans within 11 min by UPLC-MS/MS.

2.3.3 Other analytical methods

Capillary zone electrophoresis(CZE) and micellar electrokinetic chromatography(MEKC) (Farran & Ruiz, 2004) have been used by some researchers to separate phenoxy acid herbicides. Trace level analysis by electrophoresis meets some difficulties in detectors. UV-Vis(Nemoto & Lehotay, 1998) or fluorescence detector is common in the application. Besides, the process in separation with electrophoresis is greatly depending on the mobile phase (ionic strength, pH) and peak shif t sometimes is very serious, thus, quantitative analysis may be inaccurate.

Compared with instrumental separation methods, immunochemical determination technology exhibits remarkable specificity, sensitivity, rapidness and high throughput in detection. Moreover, immunochemical methods cost less and can be used in the field. I. A. Lyubavina, (Lyubavina et al., 2004) used monoclonal antibodies labeled with colloidal gold to detect 2, 4-D residues in aqueous samples.

3. Dinitroaniline herbicides

R_1 = Akyl, Halogenated hydrocarbons, Naphthenic ;

R_2 = Akyl, Halogenated hydrocarbons, Naphthenic , H；

R_3 = NH_2, H, CH_3；

R_4 = CF_3, CH_3, SO_2CH_3, SO_2NH_2, C_2-C_4 Akyl；
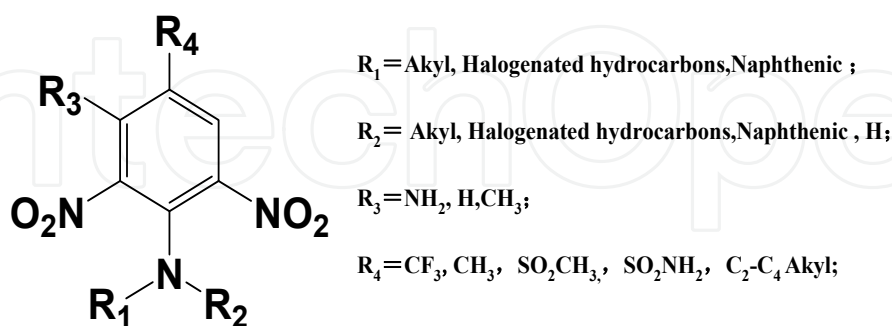
Fig. 2. Chemical structure for dinitroaniline herbicides

Dinitroaniline herbicides are used to control some broad-leaved weeds and the major annual grasses(García-Valcárcel et al., 1996). There are two classes of dinitroaniline herbicides depending on different substituents at R^4 site (Fig 2). The R_4 is alkyl or halogenated hydrocarbon for class I dinitroaniline herbicides, that is methyl aniline herbicide. Trifluralin, pendimethalin and ethalfluralin are typical methyl aniline herbicides.

For class II, the R4 group contains sulfone structure and nitralin belongs to this class. Some toxicological experiments showed that dinitroaniline herbicides exhibits carcinogenicity and impaired the normal function of organs. MRLs of some dinitroaniline herbicides in agricutural products were listed in table 5.

3.1 Sample preparation

Because of the strong polarity of dinitroaniline herbicides, some slightly polarity organic solvents such as acetonitrile, methanol and acetic ether are most applied to extract these herbicides from various matrix by a single or mixed manner. Few reports were found using single non-polar solvents (e. g. n-hexane). For extraction procedure, MASE, SFE, sonication and pressurized liquid extraction (PLE) are reported (table 6). Some analysts applied solid phase microextraction (SPME), which is intensively used in headspace analysis, to analyze dinitroaniline herbicides, but recoveries were poor.

In nitrobenzene herbicide pre-treatment methods, SPE technique was used more often. Commonly used stationary phase was based on florisil and C_{18} sorbents depending on different nature of the targeted compounds and matrix. Florisil maily was used for removing lipophilic interfences in purification (Huo et al., 2006) procedure and usually florisil (25g, previously activated with 3% H_2O) can adsorbed 1g fat), so particularly suitable for oily substances Florisil. Some reports have showed that good purification effects (the average recovery rate was 74% or more) using florisil in cleanup step in food analysis. Another material - C_{18} sorbent is also widely used in purification step. Darcy D. Shackelford (Shackelford et al., 2000) successfully applied C_{18} sorbent to remove co-extracts in analysis (recovery> 80%)

3.2 Detection

In the residue analysis of dinitroaniline herbicides, chromatography detection was dominant, especially GC with high sensitivity and good separation effects based on the summary of recent 20 year literature. Detectors such as ECD, FID, NPD and MS were used widely (see table 7)

Herbicide	Agricultural product	USA	Japan	China	Canada	New Zealand	South Korea
Trifluralin	Grains, fruits, vegetables and vegetable oil	0.05	0.15	0.05-0.15	0.5	0.03	0.05
pendimethalin	Drinking water, fruits, nuts, vegetables	0.1	0.2	0.2	-	0.02	-
Benfluralin	Peanuts, lettuce	0.05	-	-	-	-	-
ethalfluralin	Soybean, peanuts, Sunflower seeds	0.05	-	-	-	-	-
Oryzalin	Apples, kiwi fruits, Pan pomegranate and drinking water	0.05	0.05-0.2	-	-	0.4	-

Table 5. MRLs of some dinitroaniline herbicides (mg/kg)

Matrix	Solvents for extraction	Cleanup	Recovery %
Carrots and fruit	Hexane + acetic ether (1:1)	SPE (Florisil)	—
Fruits, nuts, vegetables	Methanol, methanol-water, 2 - propionaldehyde and n-hexane	GPC& SPE（florisil）	72-126
Industrial wastewater and urban domestic water	Dichloromethane	—	73-99
Soil	Acetonitrile-water	SPE(Florisil)	90-120
Soil, plants and air	Methanol, acetic ether	SPE(Florisil)	75
Blood, urea and water	SPME	—	35-64
Peanuts	Methanol, Dichloromethane	SPE(Florisil)	75.6-80.4
Banana, cucumber, apple, lettuce and oranges	Acetonitrile	SPE(C$_{18}$)	70-120
River water	-	SPE	>80
Canola seed, crude powder and Refined oil	Acetonitrile	SPE(C$_{18}$)	89-96
Fruits and Vegetables	Acetonitrile	SPE	85-101
Soil	Acetone - water - acetic acid	—	96.6
Soil, water	Ether	SPE (C$_{18}$)	89-104
water	-	SPE	50-77
Soil	Acetonitrile	—	—
Juice	Methanol	SPE (C18)	93.8～99.5
Buckwheat	n-hexane	SPE(Florisil)	>74

Table 6. Extraction and cleanup of initroaniline Herbicides

Targeted compounds	Analytical measure	Limit of Detection (LOD)	Ref
Benfluralin, Trifluralin	GC/FID	—	(Boyd-Boland & Pawliszyn, 1995)
Trifluralin, Benfluralin, ethalfluralin, isopropalin,	GC/ECD	0.01mg/kg	(West et al., 1988)
Benfluralin, ethalfluralin, isopropalin, profluralin, pendimethalin, fluchlorlin	GC/ECD	0.1 ng/mL (water, urea) 1 mg/mL(blood)	(Guan et al., 1998)
pendimethalin	GC/NPD	0.01 ppm (soil) 0.1 ppb(water)	(Sanchez-Brunete et al., 1994)
Trifluralin, ethalfluralin, profluralin,	GC/ECD	-	(Hsu et al., 1991)
Trifluralin	GC/ECD	2.5 pg/uL	(D'Amato, 1993)
pendimethalin	GC/ECD	0.022-0.045 mg /kg	(Engebretson et al., 2001)
pendimethalin	GC/NPD	0.1-4.4 µg/kg	(Fenoll José et al., 2007)
Trifluralin	GC/ECD	-	(Cessna & Kerr, 1993)
Trifluralin	Electrochemical analysis	2×10^{-9} mol/L	(Wen et al., 2008)
Benfluralin, pendimethalin, Trifluralin	GC/MS	0.05 -0.1mg /kg	(Tanabe et al., 1996)
Ethalfluralin, Trifluralin	GC/MS	0.1-4.6 ug/L	(Albero et al., 2005)
ethalfluralin, Benfluralin dinitramine	GC/MS GC/NPD	0.001-0.02 ug/ g	(Sánchez-Brunete et al., 1998)
Trifluralin, ethalfluralin, pendimethalin, isopropalin	HPLC/UV	0.5µg/kg-0.02mg/kg	(Cabras et al., 1991)
Trifluralin, ethalfluralin, pendimethalin	HPLC/ UV	0.09-0.14ug/L	(Vitali et al., 1994)
nitralin	HPLC- UV	6.9 ng	(Ruiz de Erenchun et al., 1997)
Trifluralin	HPLC/ UV	1µg/kg	(Topuz et al., 2005)
Trifluralin	HPLC/ UV	0.025mg/kg	(Huang et al., 2004)
Trifluralin	ELISA	0.1-100ng/mL	(Gyöngyvér et al., 2000)
Trifluralin	Immunosensor	2×10^{-17}-3×10^{-5} ng/mL	(Szendr et al., 2003)

Table 7. Summary of analytical methods for dinitroaniline herbicides

4. Sulfonylurea herbicides

Sulfonylurea herbicides are one of the largest families of herbicides in the world. DuPont company first reported the herbicidal activity of sulfonylurea compounds and the first sulfonylurea herbicide- chlorsulfuron was marketed in 1976, which opened the era of super-efficient herbicide application(Mughari et al., 2007). Now the number of the patents related to sulfonylurea herbicides is more than 400. The information of some common sulfonylurea herbicides was shown in table 8.

These herbicides, which have low toxicity to mammals, are highly toxic to plants and, consequently, are used at low application rates (3-40 g ha^{-1}). The general structure of the sulfonylurea herbicides (R-SO2NH-CONH-R, fig) consists of two R groups attached to either side of the sulfonylurea linkage (fig 3). The R group attached to the sulfur atom of the sulfonyl moiety can be an aliphatic, aromatic, or heterocyclic group, whereas that attached to the terminal nitrogen atom of the urea moiety can be a substituted triazine or pyrimidine ring.

In recent years, sulfonylurea herbicides have become very popular worldwide because of their low application rates, low toxicity to mammals, and unprecedented herbicidal activity. These herbicides are non-volatile, and their water solubilities are pH dependent being greater in alkaline than in acidic solution

$X=N, CH$
$Y=Cl, F, Br, CH_3, COOCH_3, SO_2CH_3, SCH_3, SO_2N(CH_3)2$
$, CF_3, CH_2Cl, OCH_3, OCF_3, NO_2$
$R=CH_3, Alkyl$
$R_1=CH_3, Cl$
$R_2=OCH, CH_3, Cl$
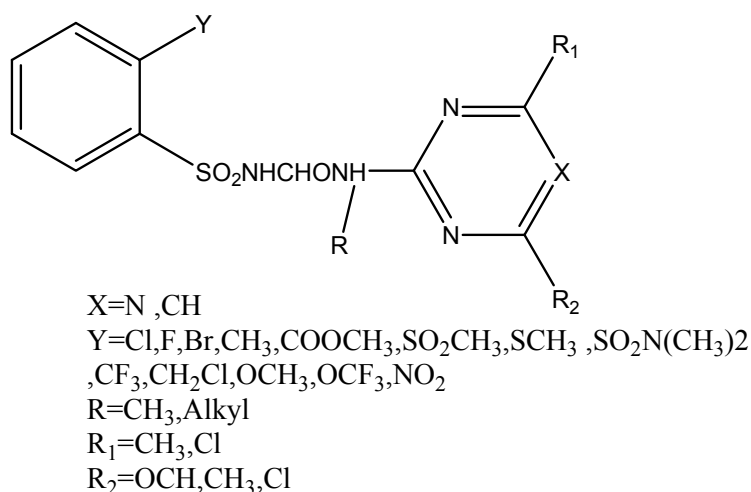
Fig. 3. Parent chemical structure of Sulfonylurea herbicides

4.1 Sample preparation

As weak acids, sulfonylurea herbicides show a more rapid degradation in environment. Therefore, the concentration of this class herbicides usually found in environmental and food samples is about 100-1000-fold lower as compared to other herbicides. Generally, the trace analysis of complex environmental and food samples needs pretreatment steps in order to reduce matrix interferences and enrich trace level analytes.

Traditional liquid-liquid extraction (LLE) or more rapid and economic solid phase extraction (SPE) or dispersive solid phase extraction (DSPE) have been reported in sulfonylurea herbicide detection. Materials such as RP-C$_{18}$, ion exchangers, mixed mode phases, graphitized carbon, and polystyrene divinylbenzene supports have been shown to be valuable sorbents for sample enrichment of various sulfonylurea herbicides in different matrix. Acidified organic solvents such as acetonitrile, dichloromethane, ethyl acetate (pH=2) were often used to extract sulfonylurea herbicides from various matrix (table 9).

sulfonylureas herbicides	Structures	molecular formula	MW	pKa
oxasulfuron		$C_{17}H_{18}N_4O_6S$	406.4	5.1
thifensulfuron-methyl		$C_{12}H_{13}N_5O_6S_2$	387.4	4.0
metsulfuron-methyl		$C_{14}H_{15}N_5O_6S$	381.4	3.3
triasulfuron		$C_{14}H_{16}ClN_5O_5S$	401.8	4.6
chlorsulfuron		$C_{12}H_{12}ClN_5O_4S$	357.8	3.6
bensulfuron-methyl		$C_{16}H_{18}N_4O_7S$	410.4	5.2
prosulfuron		$C_{15}H_{16}F_3N_5O_4S$	419.4	3.8
pyrazosulfuron-methyl		$C_{14}H_{18}N_6O_7S$	414.4	3.7
chlorimuron-ethyl		$C_{15}H_{15}N_4O_6S$	414.8	4.2
primisufuron-methyl		$C_{15}H_{12}F_4N_4O_7S$	468.3	5.1

Table 8. Infromation for some Sulfonylurea herbicides

Matrix	Herbicide	Extraction	Clean-up	Ref.
Carrots	Linuron	Hexane–diethyl ether, homogeniser	Florisil cartridge	(D'Amato, 1993)
Potatoes	Linuron	Acetone, homogeniser	LLE–Silica cartridge	(Miliadis & Vasilikiotis, 1990)
Cereals	Metsulfuron	Methanol, homogeniser	Liquid chromatography	(Zhou et al., 1994)
Rice	Bensulfuron	Methylene chloride, homogeniser	Silica cartridge	(Zhou et al., 1996)
Carrots	Linuron	Water (acidic pH), shaking	-	(Sojo et al., 1997)
Garlic	Linuron	Methanol, homogeniser	Alumina column	(Cessna, 1991a)
Asparagus	Linuron	Methanol, homogeniser	LLE–Florisil column	(Cessna, 1990)
Cereals	Chlortoluron	Ethanol–water, homogeniser	Silica column	(Pérez et al., 1993)
Potatoes	Isoproturon	Methanol, homogeniser	–	(Yaduraju, 1993)
Grains	Sulfonylureas	Acetonitrile, homogeniser	Cation–exchange cartridge	(Krynitsky & Swineford, 1995)
Potatoes	Linuron	Acetone, homogeniser	LLE–Florisil column	(Mattern, 1989)
Grains, cereals	Chlorsulfuron	Ethyl acetate, blender	LLE–GPC	(Slates, 1983)

Table 9. Extraction and clean-up for sulfonylurea herbicides

In order to determine the multiresidue of oxasulfuron, thifensulfuron-methyl, metsulfuron-methyl, triasulfuron, chlorsulfuron, bensulfuron-methyl, prosulfuron, pyrazosulfuron-methyl, chlorimuron-ethyl and primisufuron-methyl in soybeans, Qi tried various solvent system including acteone, acetonitrile, dichloromethane, ethyl acetate to optimize the extraction procedure. It showed that the serious emulsification occured when using dichloromethane and more interferences were extracted by acteone and ethyl acetate. Finally, they used acetonitrile to extract these compounds from soybean. For clean-up step, Qi tested the purification effects of SPE packed with different materials (C$_{18}$ 500mg, Florisil 1000mg &3000mg, Al$_2$O$_3$-Neutral 500mg &1000mg) and satisfied results were obtained when using SPE columns packed with Florisil (3000mg).

4.2 Detection

Various methods for sulfonylurea herbicide determination have been published up to now. These compounds are not directly amenable to GC, because of their low volatility and thermal instability. Few is reported by GC analysis after derivatization.

Most of the applications known are based on HPLC using reversed phase columns followed either by ultraviolet (UV) or mass spectrometric (MS) detection. The typical conditions for HPLC separation were set as follows (table 10):

Column: C_{18} (250*4.6mm i.d., 5.0μm), temperature 45 °C; UV wavelength: 230nm
Mobile –phase: acetonitrile-water (pH=2.5, adjusted with 85% phosphoric acid); flow rate: 1.0mL/min
The gradient elution program of HPLC separate condition (table). Qi (Qi et al., 2004)applied this procedure to analyze the sulfonylurea herbicide residues in soybean samples.

Time (min)	Water acidfied with Phosphoric acid (pH=2.5)%	acetonitrile (%)
0.00	80	20
1.75	65	35
10.00	60	40
13.00	50	50
15.00	40	60
22.00	40	60
22.01	10	90
27.00	10	90

Table 10. Gradient elution program for HPLC

5. Triazine herbicides

Triazine herbicides are a class of herbicides used for protecting crops from weeds before emergence or during early stage after emergence. The history of their use can be traced back to1952 when J. R. Geogy synthesized and screened the first triazine derivatives. A great triazine herbicides are derived from *s*-triazine (fig 4) For R1 position, this is most often –Cl(the commercial names ending with ~azine), -SCH3(-tryn) and -OCH3(-ton). The substitunts at R2 or R3 are usually amino groups. (See table 1)

Triazines and their degradation products are toxic and persistent in water, soil and organisms(Vitali et al., 1994). Moreover, atrazine is a member of the triazine family and has been classified as human carcinogen(Dean et al., 1996). From the view of their ecological and health hazards in use, some triazine herbicides have been banned in certain countries (e. g. atrazine banned to use in 1991, Germany). In the EU, the maximum allowed limit for each individual herbicide has been set at 0.1 ugL^{-1}, but the EPA of USA has set the maximum allowable level of atrazine at $3ug/L^{-1}$.
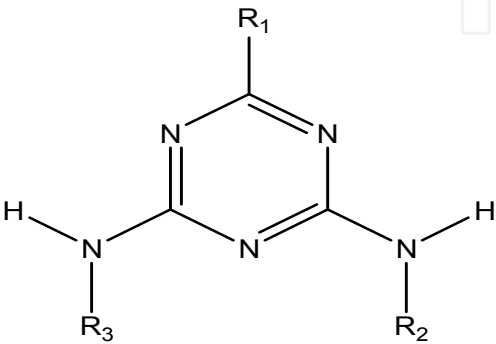
Fig. 4. Chemical structure for triazines

Compound	Substituents			Partition coefficient between octanol and water $\lg P_{OC/W}$
	R_1	R_2	R_3	
Simazine	Cl	NHC_2H_5	NHC_2H_5	2.3
Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	2.7
Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	2.91
Terbutylazine	Cl	NHC_2H_5	$NHC(CH_3)_3$	3.06
Trietazine	Cl	NHC_2H_5	$N(C_2H_5)_2$	3.07
Ipazine	Cl	$N(C_2H_5)_2$	$NHCH(CH_3)_2$	-
Deethylatrazine	Cl	NH_2	$NHCH(CH_3)_2$	1.6
Deisopropylatrazine	Cl	NHC_2H_5	NH_2	1.2
Deethyldeisopropylatrazine	Cl	NH_2	NH_2	0
Hydroxysimazine	OH	NHC_2H_5	NHC_2H_5	-
Hydroxyatrazine	OH	NHC_2H_5	$NHCH(CH_3)_2$	1.4
Hydroxypropazine	OH	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	-
Hydroxydeethylatrazine	OH	NH_2	$NHCH(CH_3)_2$	0.2
Hydroxydeisopropylatrazine	OH	NHC_2H_5	NH_2	-0.1
Simeton	OCH	NHC_2H_5	NHC_2H_5	-
Atrazon	OCH	NHC_2H_5	$NHCH(CH_3)_2$	2.69
Desmetryn	SCH_3	$NHCH_3$	$NHCH(CH_3)_2$	-
Simetryn	SCH_3	NHC_2H_5	NHC_2H_5	2.8
Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	3.07
Prometryn	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	3.34
Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	3.74

Table 11. Information for some triazine herbicides

5.1 Sample preparation

Numerous methods have also been published that examine a large variety of the triazines in many different matrices. Usually, the targeted compounds are extracted from foods by mechanical shaking or homogenisation with organic solvents, then clean-up of the extracts is carried out on SPE columns(Florisil, silica, alumina, cation-exchange cartridge). Triazine compounds are organic bases and very easy to be absorbed by cation exchange resin.

For the great differences in physical and chemical properties of different triazine herbicides, a wide array of solvents (acetone, ethanol, ether, chloroform, methanol, water et. c) have been used in analytical method development. (see table 12)

5.2 Detection

Different analytical methods, such as GC, HPLC and capillary electrophoresis, have been developed for the separation and quantification of triazine herbicides (table 13). Gas chromatography mainly with ECD, NPD and MS detection has been extensively employed for the measurement of triazine herbicide residues. DB-5 capillary column (5 % polydiphenyl- and 95 % polydimethylsiloxane; 30 m x 0.25 mm, film thickness 0.25 μm) or its analogue is suitable for triazine analysis.

Matrix	Herbicide	Extraction	Clean-up	Ref.
Vegetables, rye	Triazines	Dichloromethane maceration, shaker	Silica column	(Roseboom & Herbold, 1980)
Cereals, apples, celery	Triazines	Methanol, blender	LLE–Cation-exchange cartridge	(Pardue, 1995)
Vegetables	Triazines	Acetonitrile–water, homogeniser	Carbopack cartridge SCX column	(Battista et al., 1989)
Corn, vegetables, sugar beet	Simazine	Water, homogeniser Chloroform, shaker	Alumina column	(Pringle et al., 1978)
Cereals, vegetables	Metribuzine	Acetonitrile–water, reflux	LLE–Florisil column	(Thornton & Stanley, 1977)
Potatoes	Metribuzine	Water, steam distillation	LLE–Silica column	(Ohms, 1976)
Fruits, vegetables	Atrazine	Ethyl acetate, shaker	C18 column	(Wittmann & Hock, 1993)
Grape juice	Simazine	Diethyl ether (acidic pH), shaker	-	(Ortiz-Gomez et al., 1995)
Oil	Simazine	Acetonitrile, blender	-	(Montiel & Sánchez, 1996)
Olives	Simazine	Ethyl acetate, blender	-	(Cessna & Benoit, 1992)
Onions	Cyanazine	Ethanol–water, homogeniser	LLE–Florisil column	(Bailey et al., 1978)
Vegetables	Triazines	Acetone, blender	LLE–Florisil column	(Lawrence & Laver, 1974)
Cereals, fruits, vegetables	Triazines	Methanol, blender	Alumina column	(Mortimer et al., 1994)

Table 12. Extraction and clean-up for triazine herbicides

Tomkins and Ilgner (Tomkins & Ilgner, 2002) developed a GC-MS method for the detection of triazine herbicides (atrazine, cyanazine, simazine) and their decomposition products (deethylatrazine, deisopropylatrazine) in environmental waters. Balduini (Balduini et al., 2003) meaured the triazine herbicides in breast milk. Five triazines were adsorbed on a graphitized carbon black SPE cartridge, desorbed and analysed by GC/MS. Detection and quantification limits were 0.3 and 1 ppb from 1 mL of breast milk. Some triazine herbicides and their degradation products have been separated by reversed phase HPLC, and their atmospheric pressure chemical ionization (APCI) or electrospray mass spectra were measured. The APCI technique gives primarily [M+H]+ ions, but fragment ions are observed with electrospray and conditions that favor CID The LC/MS techniques are

Matrix	Herbicide	Analytical measure	LOD	Ref
Corn	Atrazine	GC-ECD	0.002 ppm	(Pylypiw et al., 1993)
Onion	Cyanazine	GC-NPD HP-1 Column	10 mg/kg	(Cessna, 1992)
Cereals, vegetables	Metribuzin	GC-ECD OV-225 Column	0.01 mg/g	(Ohms, 1976; Thornton & Stanley, 1977)
Vegetables, corn, sugar beet Oil, olives	Simazine	GC-NPD OV-101 Column HP-1 Column	mg/kg 0.01 ppm	(Pringle et al., 1978; Montiel & Sánchez, 1996)
Rye, vegetables Cereals, celery, apples	Triazines	GC-NPD Carbowax 20 M; OV-225 DB-17	0.01–0.02 mg/kg 0.02–1.0 ppm	(Roseboom & Herbold, 1980)
Breast milk	Triazines	GC-MS BPX-5 SGE	0.3-1 ppb	(Pardue, 1995)
Tap water, rice, maize and onion	Triazines	GC/MS CP-Sil 5 CB GC-FID CP-Sil 8 CB,	- 14-74 ngmL^{-1}	(Bailey et al., 1978)
Oranges, corn	Atrazine	HPLC Reversed-phase C18 Methanol–water UV 230 nm	0.015–0.300 ppm	(Wittmann & Hock, 1993)
Blueberries	Simazine	HPLC Reversed-phase C18 Acetonitrile–water UV	0.08–0.17 ppm	(Ely et al., 1993)
Grape juice	Simazine	HPLC Reversed-phase C18 Methanol–acetate buffer pH 5.0 UV 230 nm	20 mg/ L	(Ortiz-Gomez et al., 1995)
Vegetables	Triazines	HPLC Reversed-phase C18 Acetonitrile–phosphate buffer pH 6.7 UV 220 nm	10 ng/g	(Battista et al., 1989)
Oysters	Triazines	HPLC-MS/MS	-	(Wittmann & Hock, 1993)
Sediments and water	Triazines	HPLC-APCI-MS/MS	-	(Takats et al., 2001)
-	Triazines	ELISA	<1 ppb.	(Wittmann & Hock, 1993)
Surface water	Simazine	SPFIA	1.3±0.9 ngmL^{-1}	(Bruun et al., 2001)

Table 13. Extracton and cleanup for triazine herbicides

appropriate for triazine metabolites and their degradation products that are not amenable to GC/MS, but they may not provide advantages over GC/MS for most triazine herbicides and their dealkylated degradation products that are amenable to GC/MS. Hammock 's lab (Wortberg et al., 1995)developed immunoassy to detect four triazines in 1995 and the LOD of the ELISA was lower than 1ppb. Herranz (Herranz et al., 2008) developed solid-phase fluorescence immnunoassay (SPFIA) and applied it in simazine detection of surface water with higher sensitivity (LOD 1.3±0.9 ng/mL).

6. Amide herbicides

Amides, especially of chloroacetic acid and substituted anilines, have been and are popular herbicides since the first amide herbicide-allidochlor was found 60 years ago. Acetochlor, alachlor, butachlor, dimethenamid, metolachlor, and propachlor are amides of chloroacetic acid, and especially acetochlor, is used widely in the world for its high efficiency as the treatment agents before emergence. They are also in the list of chemical pollutants that need to be more heavily monitored due to their toxicity and accumulation in environment and their effects on the environment and human health. Acetochlor was listed as B-2 carcinogen by EPA (USA). Other acids used to form the amides include propanoic acid and several substituted benzoic acids(Nartova et al., 2008). An alkyl or alkyloxyalkyl group is usually substituted for the other hydrogen of the amide nitrogen. Some representative amide herbicides are shown in table 14.
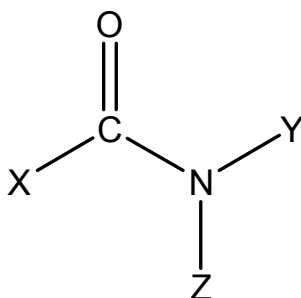
Fig. 5. Parent strucutre for amide herbicides

6.1 Sample pretreatment

For extraction of amide herbicides from food or agricultural products, solvents such as acetone, acetone-water, petroleum ether or acetonitrile were used widely (table 15). A typical sample treatment procedure was as follows: sample was extracted by acetone, then sulfate solution was added to the extracts, and finally LLE procedure was carried out with petroleum ether. But, the LLE isn't suitable for purification of some polar compounds (e. g. alachlor). For complex samples, further clean-up process is needed, usually based on SPE (florisil, alumina, silica or carbopack cartridge). C_{18} sorbents mainly used for the clean up of water samples before analysis solid-phase microextraction (SPME) considered as solventless analytical techniques, has been reported to detect the acetochlor, alachlor, and metolachlor residues in water samples.

6.2 Detection

GC was the most common method to detect the amide herbicides, usually equipped with selective detectors such as ECD, NPD or MS (Li et al., 2006). Acetochlor often can't be
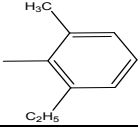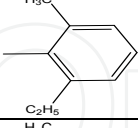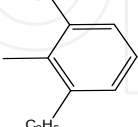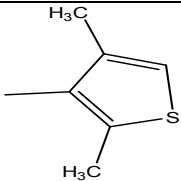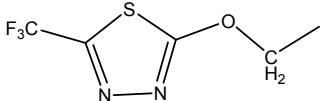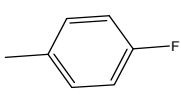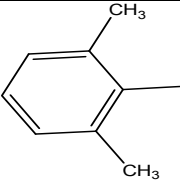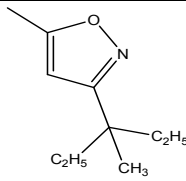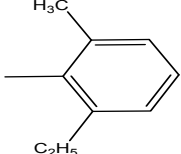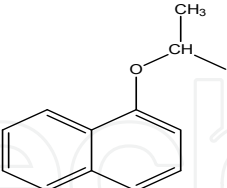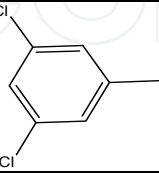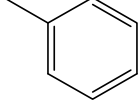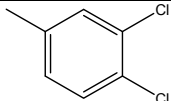
Name	X	Y	Z
Acetochlor	-CH$_2$Cl		-CH$_2$OCH$_2$CH$_3$
Alachlor	-CH$_2$Cl		-CH$_2$OCH$_3$
Butachlor	-CH$_2$Cl		-CH$_2$O(CH$_2$)$_3$CH$_3$
Dimethachlor	-CH$_2$Cl		-CH(CH$_3$)CH$_2$OCH$_3$
Flufenacet			- CH(CH$_3$)$_2$
Isoxaben			-H
Metolachlor	-CH$_2$Cl		-CH(CH$_3$)CH$_2$OCH$_3$
Napropamide		-C$_2$H$_5$	-C$_2$H$_5$
Pronamide		-C(CH$_3$)$_2$C≡CH	-H
Propachlor	-CH$_2$Cl		- CH(CH$_3$)$_2$
Propanil	-C$_2$H$_5$		-H

Table 14. Information for some amide herbicides

separated with atrazine on the capillary column and thus, some analysts used NPD connected with ECD to realize the simutanious detection of the two compounds. What's more, the heated decomposition temperature of some amide herbicdes is low (metolachlor, 105 °C), which makes difficulties in detection of these compounds by GC.

The HPLC method, based on reversed phase C_{18} or C_8 column, came into being. The mobile phase often was methanol-water or acetonitrile-water (pH 3, adjusted with acetic acid). MS-MS techqiues further improved the analytical selectivity. Steeen, (Ling et al., 2006)used GC-MS/MS to detect the pesticide redidues in marine system with LOD ranging from 0.2 to 0.5 ng/L. Striley(Striley et al., 1999) developed ELISA to measure the putative major human metabolite of metolachlor, metolachlor mercapturate (MM) in human urea. Tessier, (Tessier & Marshall, 1998) developed immunoassay to detect alachlor in aqueous samples. Yakovleva, (Szendr et al., 2003) established ELISA and applied to analyze butachlor residues in mineral, ground and surface water. Other application of detection method was listed in table 16.

Matrix	Herbicide	Extraction	Clean-up	Ref
Tamotoes	metolachlor	Water(acidic pH), homogeniser	LLE	(Gaynor et al., 1993)
Carrots	metolachlor	Water(acidic pH), shaker	-	(Sojo et al., 1997)
Potatoes	metolachlor	Acetone-hexane, blender	LLE	(Singh, 1997)
Cereals	Chloroacetamides	Acetonitrile, homogeniser	LLE-florisil column	(Balinova, 1988)
Vegetables	metolachlor	Methanol, blender	LLE-silica cartridge	(Gaynor et al., 1992)
Tea leaves	Amide herbicides	ethyl acetate, shaker	An active carbon SPE column connected to a Florisil column	(Shen et al., 2007)
Soybean	Amide herbicides	Acetone, shaker	Florisil cartridge	(Li et al., 2006)
Onion	Amide herbicides	Acetonitrile microwave-assisted extraction(MAE)	Florisil cartridge	(Hans-Jürgen & Manfred, 1993)
Water	Amide herbicides	SPME	-	(Sauret-Szczepanski et al., 2006)
Water	Amide herbicides	water–acetonitrile MAE		(Fuentes et al., 2006)

Table 15. Extraction and clean-up for amide herbicides

Matrix	Herbicide	Analytical Method	LOD	Ref
Peanut, cereals	Alachlor	NPD, UC-W98	0.02–0.05 ug/g	(Conkin et al., 1978)
Corn	Alachlor, metolachlor	ECD	0.002 ppm	(Pylypiw et al., 1993)
Tomatoes	Metolachlor	Hydrolysis MS Supelcowax	10- 50 ppb	(Ely et al., 1993)
Potatoes	Metolachlor	ECD, OV-1	0.15 ng	(Gaynor et al., 1992)
Potatoes, tomatoes, maize	Chloroacetamides	ECD QF-11DC-200, Apiezon L	0.02–0.05 ng	(Singh, 1997)
Tea leaves	Amide herbicies	GC-NCI-MS GC-EI-MS	<2 ug/kg	(Balinova, 1988)
Soybean	Amide herbicies	HPLC-UV, C_{18} 210 nm	1-7.2 ppb	(Li et al., 2006)
Carrots	metolachlor	HPLC-UV 220nm	--	(Sojo et al., 1997)

Table 16. analytical methods for some amide hericides

7. Glyphosate

Glyphosate is the common name for *N*-(phosphonomethyl)-glycine, a total-kill herbicide (first found its herbicidal activity in 1971, introduced in 1974 by theMonsanto Company under the trade name "Roundup" and rapidly became one of leading herbicides in the world.), having the environmental advantages of low mammalian toxicity and rapid breakdown in the soil leaving no harmful residues. Having pKa values of 0.78, 2.29, 5.96 and 10.98, glyphosate is a very polar and amphoteric compound(fig 6).

Glyphosate is used to control grasses, herbaceous plants including deep rooted perennial weeds, brush, some broadleaf trees and shrubs, and some conifers(Tsui et al., 2005). Glyphosate does not control all broadleaf woody plants. Glyphosate applied to foliage is absorbed by leaves and rapidly moves through the plant. It acts by preventing the plant from producing an essential amino acid. This reduces the production of protein in the plant, and inhibits plant growth. Glyphosate is metabolized or broken down by some plants, while other plants do not break it down. Glyphosate dissolves easily in water. Aminomethylphosphonic acid (AMPA) is the main break-down product of glyphosate in plants (Zhao et al., 2009).
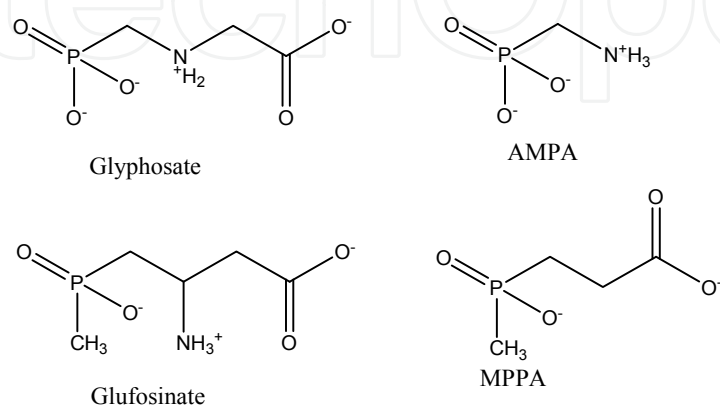

Fig. 6. Chemical structure for glyphosate, glufosinate and their main metabolites

Glufosinate [DL-homoalanine-4-yl(methyl)phosphinic acid], is another highly polar amino acid herbicides. A major breakdown product of glufosinate found in both plants and animals that have been exposed to glufosinate is 3-methylphosphinicopropioninc acid (MPPA) (Moye et al., 1983).

Based on the results of animal studies, glyphosate does not cause genetic damage or birth defects, and has little or no effect on fertility, reproduction, or development of offspring. There is not enough information available at this time to determine whether glyphosate causes cancer. There have been no reported cases of long term health effects in humans due to glyphosate exposure (Tsui et al., 2005). The Food and Agriculture Organization (FAO) of the United Nations has set a maximum residue limit (MRL) of glyphosate in wheat at 5 mg/kg. The world health organism evaluated glyphosate on its acceptable daily intake value and the data allocated for glyphosate was 0.3 mg/kg body mass.

7.1 Sample preparation

The main problem in glyphosate and its metabolite analysis is their recovery from biological or field samples. Glyphosate is a highly polar herbicide, very soluble in water and insoluble in most organic solvents, which does not allow extraction with organic solvents and makes the extraction difficult and the preconcentration step quite lengthy.

Due to the amphoteric character of glyphosate and AMPA, both anionic and cationic resins have been used for preconcentration and clean-up purposes. Another important aspect to be considered is the binding of glyphosate to organic matter. Some reports showed that humic substances adsorb glyphosate strongly because the hydrogen bonding interactions between the hydrogen acidic and the oxygen group of both substances. Glyphosate extraction is usually carried out with water or water with chloroform, sometimes at acidic pH (table 17). In this procedure, other water soluble components of foods, like amino acids, amino sugars, etc. are also extracted. These compounds interfere in the glyphosate determination making necessary the clean-up of extracts. More often used in this purification step is LLE or column chromatography on ion exchange columns.

7.2 Detection

Due to their very polar, and in most cases ionic character, Analytical methods for the analysis of glyphosate and its major metabolite, AMPA, include thin-layer chromatography, capillary electrophoresis (CE), gas (GC) and liquid chromatography (LC) after derivatisation.

The availability of derivatisation techniques compatible with an aqueous extract or sample and the chromatographic separation makes LC an attractive technique. However, for LC with conventional detection systems, such as UV-Vis or fluorescence detectors, glyphosate and AMPA need to be derivatised because of the lack of chromophore or fluorophore. Three different procedures are generally used for the determination of glyphosate with LC: (i) post-column ninhydrin derivatisation and UV detection; (ii) post-column fluorogenic labeling with o-phthalaldehyde and mercaptoethanol after oxidation of glyphosate to glycine; (iii) pre-column derivatization using 9-fluorenylmethyl chloroformate (FMOC-Cl) with fluorescence detection(FLD).

Post-column derivatisation was used in most of the previous studies for glyphosate analysis in water and has also been recommended by the US Environmental Protection Agency (EPA). Moyne and Boning were the first to use the FMOC-Cl reaction for derivatising glyphosate. A disadvantage of this reaction, however, is its reactivity with water, which

Matrix	Extraction	Clean-up	Ref.
Corn, fruits, soybeans	Water, blender	LLE–Cation-exchange column	(Alferness & Iwata, 1994)
Blueberries	Water, homogeniser	LLE–GPC–Cation-exchange column	(Guinivan, 1982)
Legumes, cereals	Water–chloroform, shaker	LLE–Cation-exchange column–Anion-exchange column	(Wigfield & Lanouette, 1991; Wigfield & Lanouette, 1991)
Fruits, field pea, barley and flax seed	0.1 M HCl–chloroform, blender	LLE–Ligand-exchange column–Anion-exchange column	(Cowell et al., 1986) (Cessna, 2002)
Berries	Water–chloroform, blender	LLE–Charcoal–Cation-exchange column	(Konar & Roy, 1990)
Kiwi fruit, asparagus	Water–chloroform, blender	LLE–Anion-exchange column–GPC	(Benfenati et al., 2006)
fruit juices	-	-	(Cláudia et al., 2007)
Fruits, vegetables	Water–chloroform, blender	LLE–Cation-exchange column	(Moye et al., 1983)
Cereals	Water, overnight standing extraction	100 mg C_{18} SPE	(Hogendoorn et al., 1999)
Rice, soybean sprouts	Water, acetone homogeniser	anion-exchange column Florisil Cartridge Cleanup.	(Tseng et al., 2004)

Table 17. Extraction and clean-up for glyphosate

leads to the formation of a FMOC-OH product (reaction of the acyl chloride with water) in the reaction mixture. To obtain quantitative yield in derivatisation, excess reagent has to be used. Different concentrations of FMOC-Cl have been reported in the literature for the derivatisation of glyphosate, still, there is little or no general agreement concerning the optimal molar ratio of glyphosate to FMOC-Cl to be used.

The common HPLC conditions for the separation of glyphosate and AMPA were using a single polymeric amino column and mobile phase at pH 10 which contained 55% (v/v) acetonitrile and 50mM phosphate buffer.

FMOC-OH by product make it difficult in separation by chromatography, which is represented by the large peak in front of the glyphosate chromatogram. The FMOC-OH product completely overlaps the glyphosate peak and creates difficulties in its detection (Tadeo et al., 2000). The removal of this FMOC product and separation of the glyphosate peak by column-switching technique using coupled C18 and amino columns was previously

reported. However, these silica-based columns usually degrade under high alkaline conditions. Sancho (Sancho et al., 1994). reported that a gradual decrease in efficiency of the silica-based amino column after two months' use. Ion chromatography (IC) provides a useful tool in detecting ionic substance. Zhu used ion chromatography system equipped with anion exchange column and suppressed conductivity detector to determine the gylphosate in enviromental samples with LOD 0.042 ug/mL. Patsias (Patsias et al., 2001) developed an automated method based on the on-line coupling of anion-exchange solid-phase extraction (SPE) and cation-exchange liquid chromatography followed by post-column derivatization and fluorescence detection for the trace level determination of glyphosate and its primary conversion product aminomethyl phosphonic acid (AMPA) in water.

These ionic compounds were also determined in water by liquid chromatography with mass spectrometry (LC-MS) after derivatization with FMOC, achieving quite low detection limits. The coupling of ion chromatography (IC) with electrospray mass spectrometry (ES-MS) opens new ways for the determination of polar organic micropollutants in water samples. The technique of conductivity suppress ion has been found to reduce the background signal in the range of about two-orders of magnitude leading to a significant increase in sensitivity. In addition, the formation of salt adducts has been avoided. Bauer (Bauer et al., 1999) separated glyphosate and AMPA in water on an anion-exchange column without any erivatization and detected the signal by IC-ES-MS.

The GC method can be developed to analyze glyphosate through the preparation of N-heptafluorobutyrychloroethyl   ester,   N-trifluoroacetyltrifluoroalkyl   ester,   N-trifluoroacetylheptafluorobutyl ester and tert-butyldimethylsilyl derivatives. However, it is a time-consuming procdeure to prepare the derivatives under anhydrous conditions. The usual detector equipped with GC for glyphosate analysis can be flame photometric, msaa-selective detectors or the extreme sensitive electro-capture detector.

Capillary electrophoresis (Corbera et al., 2005), as an important separation technique due to its high resolving power and speed, was also reported for glyphosate anaysis. Some (Khrolenko & Wieczorek, 2005) used p-toluenesulfonyl chloride for derivatization prioe to CE separation, others (Cikalo et al., 1996) incorporates ribonucleotides into the background electrolyte to realize the indirect photometric detection. Chang (Chang & Liao, 2002) employed fluorescein as the buffer fluorophore and an argon-ion laser to induce the fluorescence background for detection of the glyphosate, AMPA, glufosinate and MPPA.

Mass spectrometry (MS) has the potential to be a rigorous direct detection method for these compounds, particularly in their ionic states. Utilising a simple microelectrospray interface, Goodwin (Goodwin et al., 2003) analyzed glyphosate, glufosinate and their metabolites on capillary electrophoresis–mass spectrometry (CE–MS) using a combination of electrical and pressure drive for interface. The observed concentration limit of detection for glyphosate in water is 1 mM and for a water–acetone extract of wheat is 2.5 mM, allowing the underivatised herbicide to be detected at 10% of the maximum residue limit in wheat.

8. Other herbicides

In addition to the above described types of herbicides, imidazolinone (imazethapyr, imazamox, imazapyr), imazapic, carbamate (isoprocarb, oxamyl, propoxur) and diphenyl ether herbicides (acifluorfen, chlornitrofen, aclonifen, bifenox and oxyfluorfen) are also popular in agricultural production.

8.1 Imidazolinone herbicides

This class of herbicide is used to protecing beans, peanuts, corn and other crops from weeds. These herbicides are used in a small amount for their long-acting effects and trace residues in soil may cause phytotoxicity on succeeding crop (Lewis et al., 2009). In 2005, canada set MRL for imazethapyr residue in soybean, 0.1mg/kg. USA regulated the MRL of imazethapyr residue in rice, 0.3 mg/kg (G/SPS/N/USA/1229). Japan set the MRLs ranging from 0.01 to 0.5 mg/kg of imazethapyr residue in foods depending on the food types.

There are carboxyl group and imino group in the chemical structure of imidazolinone herbicdie, which make imidazolinone herbicides show strong polarity, and thus the control of pH in sample extraction is critical.

Many analytical methods such as HPLC, GC-MS, LC/MS have been reported for imidazolinone herbicide detection. A typical HPLC method is as follows: the targeted molecules can be extracted from the matrix with mixed solution of ammonium bicarbonate(0.1 M, pH=5)- methanol(7:3, v/v). The extracts can be partitioned with dichloromethane and the organic layer was collected and condensed for further clean-up on cation exchange column. Separation of imidazolinone herbicides can be carried out by C_{18} column with acetonitrile-1% acetic acid as mobile phase. The detection UV length can be set 252-258 nm.

With the sensitivity and sepecificity of HPLC-MS (Chu et al., 2008), some analyzed the imidazolinone herbicides in various matrix. Under positive mode, [M+H]+ can be monitored for each compound(m/z262 for imazapyr, m/z275 for imazamethabenz acid, m/z306 for imazamox, m/z276 for imazapic, m/z290 for imazethapyr and m/z312 for imazaquin).

These compounds should be esterized before analysis by GC. Anisuzzaman (Anisuzzaman et al., 2000) detected the imidazolinone herbicides in soil, water and soybean by GC-NPD and GC-MS after synthesis of dimethyl derivatives.

8.2 Carbamate herbicides

Three classes of carbamate pesticides are known. The carbamate ester derivatives, used as insecticides (and nematocides), are generally stable and have a low vapour pressure and low water solubility. Carbamate fungicides contain a benzimidazole group. It is well known that carbamate pesticides are esters of carbamic acid, having the general structure $R_1NHC(O)OR_2$, in which R_1 and R_2 are aromatic and/or aliphatic moieties.

Carbamate herbicides (Vasilescu et al., 2005) are known to repress cell division as a consequence of their disturbing nucleic acid metabolism and protein synthesis. Clorpropham, sulfallate and phenmedipham are the representatives of this family herbicides. Some examples about extraction and clean-up of carbamates and thiocarbamates are shown in table.

The well-known thermal instability of carbamates has led to the use of HPLC, but its most usual detectors have a limited sensitivity. In the 1980s, some used post-column hydrolysis and derivatization with fluorescence detection to overcome these disadvantages. The carbamates were degraded into methylamine and then derivatized to a fluorescent isoindole product, which was widely used in carbamate residue analysis in fruits and vegetables. In addition, many references investigation showed that both ESI and/or APCI with HPLC/MS were used to analyze the carbamates and APCI can help to reduce matrix effects.

Although careful control of experimental conditions may allow direct determination of carbamates by GC, large number of experimental factors such as injector temperature, residence time in the injector, solvent nature and injection mode, are known to affect the results. Derivatization reactions are therefore required prior to GC analysis.

Matrix	Herbicide	Extraction	Clean-up	Ref.
Rice	Thiobencarb	Methanol or acetone, blender	–	(Au & Fung, 1988)
Potatoes	Chlorpropham	Tetrahydrofuran–water–acetonitrile–acetic acid, homogeniser	–	(Camire et al., 1995)
Fruits, vegetables	Chlorpropham	Methanol, blender	Alumina column	(Wilson et al., 1981)
Potatoes	Chlorpropham	Acetone, homogeniser	LLE	(Tsumura-Hasegawa et al., 1992)
Garlic	Triallate	Methanol, homogeniser	LLE–Florisil cartridges Alumina column	(Cessna, 1991b)
Potatoes	Chlorpropham	Dichloromethane (water), blender	–	(Mondy et al., 1992)
Lentils	Triallate	Acetonitrile, shaker	Alumina column	(Cessna, 1980)
Potatoes	Chlorpropham, propham	Dichloromethane (water), blender	Silica-TLC	(Corti et al., 1991)
Fruits, vegetables	Chlorpropham, propham, triallate	Ethyl acetate, homogeniser	LLE–Florisil column	(Blaicher et al., 1980)
Potatoes	Chlorpropham	Water suspension,	solid-phase microextraction	(Volante et al., 1998)
fruit and vegetables	carbamate herbicides	acetonitrile (MeCN) containing 1% acetic acid (HAc)	dispersive-SPE cleanup step (primary secondary amine+ C_{18})	(Martínez Vidal et al., 2006)

Table 18. Extraction and clean-up for some carbamate herbicides

The main derivatization reactions applied to the family of herbicides involve the N-protection for carbamates. Among them, silylation, acylation and alkylation, together with reactions of transformation into aniline have been used. An N-protection reaction for derivatization of compounds containing an NH-reactive group, based on the use of sodium hydride/dimethyl sulphoxide/methyl iodide (NaH/DMSO/CH₃I) has been frequently used.

8.3 Diphenyl ether herbicides

Among the herbicides being used, diphenylether compounds of herbicide are mainly introduced at pre- or post-emergence in controlling annual broad-leaved weeds and some types of grasses in numerous crops like rice, cereals, maize, etc(Murakami et al., 1988). This class of herbicides has proved to be an inhibitor of protoporphyrinogen oxidase, that leads to the accumulation of protoporphrin and therefore blocks the formation of chlorophyll. Molecules that inhibit protoporphyrinogen oxidase (Protox) have been among the most

frequently patented class of herbicides over the past decade. Commercial Protox inhibitors can be classified in a major chemical group, the *p*-nitrodiphenyl-ethers, commercially known as the diphenyl-ethers (DPhE).

This class of herbicides is mainly composed of esters but few compounds are acids or have an acidic behavior, with pKa comprised between 2.7 and 3.8. There are two main metabolites that arise from the degradation of the DPhE herbicides studied, bifenox acid from the hydrolysis of bifenox and acifluorfen from the degradation of lactofen and fluoroglycofen. Bifenox and oxyfluorfen are reported to be carcinogenic or suspected to be carcinogenic compounds (Sabino et al., 2004).

The herbicides in this category have a 2-chlorodiphenyl ether nucleus in common, and most also have nitro and trifluoromethyl substituents. As this class of compounds is usually nonvolatile and thermally unstable, most of the direct methods have been performed by using LC. Acifluorfen and fomesafen can be separated on a C-18 column, with a slightly acidic mobile phase, followed by electrospray to give [M-H]⁻ ions. Lactofen and oxyfluorfen were also separated on a C-18 column, but without acid in the mobile phase.

Oxyfluorfen is amenable to GC separation (Wong et al., 2003), and nitrofen, with a similar structure, should have favorable properties for GC. Shen (Shen et al., 2008) extracted DPhE from vegetables sample with acetonitrile, then the extract was cleaned up by Envi-Carb SPE column connected to Alumina Neutral SPE column, determined by gas chromatography-negative chemical ionization mass spectrometry. The lactofen esters may be amenable to GC separation, but the acid acifluorfen and the sulfonamide fomesafen require derivatization for GC.

DPhE showed good solubility in acetone and acetonitrile and both organic solvents can be miscible with water. However, acetone can extract more interferences from matrix, expecially from samples containing high fat and thus, acetonitrile is used a lot in DPhE extracting from agricutral products. Considering the polarity of DPhE, sorbents such as florisil or alumina are suitable for clean-up steps.

9. Conclusion

Food analysis entails important difficulties owing to the complexity of the sample matrix. Most methods for the analysis of pesticide residues described in the literature use a combination of some form of extraction with an organic solvent, with one or several clean-up and purification steps to remove coextractants before the sample is subjected to a further separation/detection technique.

One of the current trends of modern analytical chemistry is the miniaturization of the various tools daily used by a large number of researchers. Ultrafast separations, consumption of small amounts of both samples and reagents as well as a high sensitivity and automation are some of the most important goals desired to be achieved.

9.1 Sample treatment

Sample treatment has been recognized as the main bottleneck of the analytical process, especially when trace analysis is the purpose. For many years a large number of research laboratories and analytical instrument manufacturing companies have been investing their efforts in this field, which includes miniaturized extraction materials, sample pre-treatment procedures and separation techniques.

Solid-phase microextraction (SPME) is a relatively new technique introduced by Pawliszyn and coworkers in the early 1990s (Janusz, 1997). The feature of this technique is that it enables sample preparation and enrichment in one step. SPME is based on the partitioning of analytes between a coated fibre and a sample. The coated fibre consists of a small fused-silica rod coated with a thin layer of a sorbing material. Upon exposure to the vapour phase above a solution or upon direct immersion in the solution, a mass-transfer process begins, driven by the second law of thermodynamics, according to which the chemical potential of each compound should be equal throughout the system. If the analyte is in the gas phase and the extractant is liquid, dissolution of the gas in the liquid is the main process, and that is governed by Henry's law and Raoult's law. As solubility is the main concept, partition of the analyte between the gas and the liquid phases will take place and all variables affecting it will influence the extraction (Volante et al., 1998).

PLE (pressurized liquid extraction) is another extraction technique recently attracted considerable attention. PLE is a sample preparation technique that combines elevated temperature and pressure with liquid solvents to achieve fast and efficient extraction of the analytes from solid matrices (Marchese et al., 2009). In PLE, the variables that affect extraction efficiency are the nature of the solvent or mixture of solvents, the solvent volume/sample mass ratio, extraction pressure and temperature, the number of extraction cycles and the duration of each cycle. However, the temperature and type of solvent seem to be the two variables with the greatest bearing on the extraction process. The solvents commonly used in pesticide extraction from vegetables and fruit are acetone, n-hexane, ethyl acetate, dichloromethane and water, while those least used are acetonitrile, ethanol and 1-propanol (Nemoto & Lehotay, 1998).

Molecularly imprinted polymers (MIPs) with better specificities than those of traditional SPE adsorbents have recently been introduced as novel matrices for the extraction and clean-up of target compounds (Hu et al., 2010). To date, many papers describing the use of MIPs as SPE materials to clean-up and preconcentrate trace compounds from various matrices have been published (She et al., 2010; Baggiani et al., 2001; Sambe et al., 2007; Mhaka et al., 2009). She et al, 2010 prepared class-specific molecularly imprinted polymers for the selective extraction and determination of sulfonylurea herbicides in maize samples by high-performance liquid chromatography–tandem mass spectrometry.

9.2 Separation system

Among the separation techniques, capillary electromigration methods (which also include capillary electrochromatography, CEC), microchip and nano-LC/capillary LC have received especial attention. Besides their well known advantages over other separation tools, the role of these miniaturized techniques in food analysis is still probably in an early stage. In fact, applications in this field carried out by CEC, microchip, nano-LC and capillary LC are only a few when compared with other more established procedures such as conventional GC or HPLC (Myint et al., 2009).

In the last few years biosensors have shown great potential as analytical tools for the development of rather automatic, fast and direct analysis methods that in many cases avoid sample pretreatment or requireminimal sample preparation, allowing on-site field monitoring (Salmain et al., 2008). For example, an optical fiber based biosensor was developed for atrazine and endrine monitoring in water using *Scenedesmus subspicatus* cells, immobilized on filter paper and covered with a thin alginate layer hardened with calcium chloride(Védrine et al., 2003).

10. References

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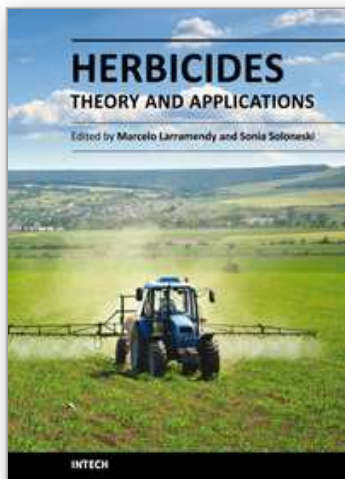
Herbicides, Theory and Applications

Edited by Prof. Marcelo Larramendy

The content selected in Herbicides, Theory and Applications is intended to provide researchers, producers and consumers of herbicides an overview of the latest scientific achievements. Although we are dealing with many diverse and different topics, we have tried to compile this "raw material" into three major sections in search of clarity and order - Weed Control and Crop Management, Analytical Techniques of Herbicide Detection and Herbicide Toxicity and Further Applications. The editors hope that this book will continue to meet the expectations and needs of all interested in the methodology of use of herbicides, weed control as well as problems related to its use, abuse and misuse.

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